

MODELING PARENT AND METABOLITE FATE AND TRANSPORT IN SUBSURFACE DRAINED FIELDS WITH DIRECTLY CONNECTED MACROPORES¹

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ABSTRACT: Few studies exist that evaluate or apply pesticide transport models based on measured parent and metabolite concentrations in fields with subsurface drainage. Furthermore, recent research suggests pesticide transport through exceedingly efficient direct connections, which occur when macropores are hydrologically connected to subsurface drains, but this connectivity has been simulated at only one field site in Allen County, Indiana. This research evaluates the Root Zone Water Quality Model (RZWQM) in simulating the transport of a parent compound and its metabolite at two subsurface drained field sites. Previous research used one of the field sites to test the original modification of the RZWQM to simulate directly connected macropores for bromide and the parent compound, but not for the metabolite. This research will evaluate RZWQM for parent/metabolite transformation and transport at this first field site, along with evaluating the model at an additional field site to evaluate whether the parameters for direct connectivity are transferable and whether model performance is consistent for the two field sites with unique soil, hydrologic, and environmental conditions. Isoxaflutole, the active ingredient in BALANCE[®] herbicide, was applied to both fields. Isoxaflutole rapidly degrades into a metabolite (RPA 202248). This research used calibrated RZWQM models for each field based on observed subsurface drain flow and/or edge of field conservative tracer concentrations in subsurface flow. The calibrated models for both field sites required a portion (approximately 2% but this fraction may require calibration) of the available water and chemical in macropore flow to be routed directly into the subsurface drains to simulate peak concentrations in edge of field subsurface drain flow shortly after chemical applications. Confirming the results from the first field site, the existing modification for directly connected macropores continually failed to predict pesticide concentrations on the recession limbs of drainage hydrographs, suggesting that the current strategy only partially accounts for direct connectivity. Thirty-year distributions of annual mass (drainage) loss of parent and metabolite in terms of percent of isoxaflutole applied suggested annual simulated percent losses of parent and metabolite (3.04 and 1.31%) no greater in drainage than losses in runoff on nondrained fields as reported in the literature.

(KEY TERMS: pesticides; vadose zone water quality; preferential flow; subsurface drainage; simulation.)

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INTRODUCTION

Subsurface drainage is common in agricultural areas with considerable pesticide use. Artificial drains achieve water quantity goals by removing excess water from the upper portion of the active root zone to prevent delayed planting, stunted plant root growth, and possibly crop failure due to excessive water stress, but concerns exist that pesticides can be transported to the drains and then into adjacent streams, rivers, and lakes (Shipitalo and Gibbs, 2000). Concerns also exist about exceedingly efficient transport pathways created by possible interconnectivity between macropores and subsurface drains. Preferential flow significantly influences the transport of solutes and pesticides in both field and laboratory studies (Steenhuis *et al.*, 1990; Munster *et al.*, 1995; Elliott *et al.*, 1998; Kladvik *et al.*, 1999; Sadeghi *et al.*, 2000). Field studies have indicated immediate breakthrough of solutes and pesticides in subsurface drainage by a few, drain-connected macropores (Steenhuis *et al.*, 1990; Rothstein *et al.*, 1996; Shalit and Steenhuis, 1996; Villholth *et al.*, 1998; Shipitalo and Gibbs, 2000).

Steenhuis *et al.* (1997) modeled preferential transport to subsurface drains using a conceptual model based on two linear reservoirs located near the soil surface and closer to the drain. Their results suggested that methods based on field averaged preferential flow characteristics are needed to model preferential flow to tile drains. Fox *et al.* (2004) proposed an express fraction (EF) parameter to account for the direct hydraulic connection between macropores and subsurface drainage in a field averaged preferential flow model called the Root Zone Water Quality Model (RZWQM). They utilized a contributing area parameter relating the percentage of macropores in direct hydraulic connection to subsurface drains. When macropore flow first reached the top of the water table, a macropore/subsurface drain EF of the water and chemical was routed directly into the subsurface drain through macropores. The remaining water and chemical was allowed to fill and mix with the layers above the water table. A larger EF corresponded to greater contribution to drainage by preferential flow. Simulating fast breakthrough by drain-connected macropores resulted in improved simulated peaks of bromide and pesticide concentrations in edge of field subsurface drain flow. Fox *et al.* (2004) evaluated their proposed subsurface drain/macropore connectivity modification at only one field site with a predominately clay soil.

Along with concerns about the rapid transport of pesticides through macropores to subsurface drains,

the significance of pesticide metabolites in the environment has become important among regulators and interest groups (Coats, 1991; Somasundaram and Coats, 1991; Ray, 2003; Shipitalo and Owens, 2003). Pesticide transformation is generally a detoxification process resulting in inert compounds; however, a growing number of currently used pesticides have transformation products that are chemically active (Somasundaram and Coats, 1991). Concerns have arisen that metabolites, along with the parent compounds, could affect nontarget, particularly aquatic, organisms. Even though numerous studies have been reported on parent/daughter simulations in the literature (Ma *et al.*, 2004), there are few evaluations of model simulations for parent/daughter fate in fields with subsurface drainage, especially with the compounds investigated in this research: isoxaflutole and its metabolite, RPA 202248 (Pallett *et al.*, 1998). In fact, few studies exist on monitoring the presence of metabolites in tile-drained watersheds (David *et al.*, 2003).

In evaluating the environmental consequences of currently used pesticides, regulatory policies require the consideration of both parent compounds and their metabolites. The difficulty in applying such regulatory policies is the lack of adequate information about the formation, transport, and degradation of metabolites (Somasundaram and Coats, 1991), especially in subsurface drained fields. Pesticide transport models provide an exceptional tool for evaluating potential environmental consequences of pesticide use due to both parent compounds and metabolites. Researchers have proposed and evaluated numerous models to simulate pesticide transport and degradation: Pesticide Root Zone Model (PRZM) (Parrish *et al.*, 1992; Mullins *et al.*, 1993; Sadeghi *et al.*, 1995; Cogger *et al.*, 1998); Ground-water Loading Effects of Agricultural Management Systems (GLEAMS) (Zacharias and Heatwole, 1994; Malone *et al.*, 1999); MACRO (Jarvis, 1995; Villholth and Jensen, 1998; Villholth *et al.*, 2000), and RZWQM (Ahuja *et al.*, 2000b; Malone *et al.*, 2001; Fox *et al.*, 2004, 2006). PRZM is included in the list of recommended regulatory models for pesticide registration and is capable of simulating fate and transport of the parent compound and as many as two daughter species (Mullins *et al.*, 1993). However, the model does not consider preferential flow and subsurface drainage.

Documentation of other regularly used pesticide transport models commonly quotes the ability to simulate sequential decay chain degradation and formation. However, the literature reports few studies evaluating pesticide transport models based on measured parent and metabolite concentrations under natural field conditions (Shipitalo and Owens, 2003; Ma *et al.*, 2004). Existing evaluations primarily focus

on pesticide transport with runoff and indicate that degradation processes are sensitive to environmental conditions. Ma *et al.* (2004) report that using single kinetic rate constants for parent-daughter product formation results in errors in individual species concentrations that increases exponentially in time.

The objectives of this research were threefold. The first objective was to evaluate the parent/daughter fate and transport component of RZWQM under subsurface drained field conditions at two field sites. The model was calibrated by adjusting soil hydraulic parameters based on observed hydrology or conservative tracer transport and then evaluated based on parent and daughter concentrations in subsurface drain flow at two field sites. Few studies exist that evaluate transport models regarding both parent compounds and metabolites in field conditions. The second objective was to evaluate the EF modification proposed by Fox *et al.* (2004) to quantify the connectivity between macropores and subsurface drainage using RZWQM. By comparing two field sites with unique soil, hydrologic, and environmental conditions, this research evaluates the transferability of the EF parameter. The question is whether the calibrated 2% EF used by Fox *et al.* (2004) is appropriate for other field sites or will users need to calibrate this parameter to site-specific field conditions. In addition, by applying the model to an additional field site, this research will determine if the performance of the model concerning predicting recession limb concentrations, which were not accurately predicted by Fox

et al. (2004), is consistent. Results from this comparison may provide strategies for further improving the EF modification. The final objective was to evaluate long-term parent compound and metabolite concentrations in edge of field subsurface drain flow. Questions exist whether parent pesticide and metabolite losses, such as isoxaflutole and RPA 202248, in edge of field subsurface drain flow are equivalent to losses from runoff at nondrained sites (Rector *et al.*, 2003).

MATERIALS AND METHODS

Field Experiments

This research focused on the fate and transport of isoxaflutole (5-cyclopropyl-1,2-oxazol-4-yl)(α,α,α -trifluoro-2-mesyl-*p*-tolyl)methanone, and its daughter product, RPA 202248-a-(cyclopropylcarbonyl)-2-(methylsulfonyl)-b-oxo-4-(trifluoromethyl) Benzenepropanenitrile, in field transport experiments at two field sites with subsurface drainage facilities. Table 1 outlines the physiochemical and environmental fate properties as measured in laboratory studies as reported by Fox *et al.* (2004). Laboratory measured properties were similar to those reported by the U.S. Environmental Protection Agency (USEPA, 1998). Isoxaflutole is registered for use on corn and ground applied using standard commercial sprayers (USEPA, 1998). Isoxaflutole

TABLE 1. Physicochemical and Environmental Fate Properties for Isoxaflutole and Its Metabolite (RPA 202248).

	Isoxaflutole	RPA 202248
CAS Number	141112-29-0	143701-75-1
Chemical Name	(5-cyclopropyl-4-isoxazolyl) [2-(methylsulfonyl)-4- (trifluoromethyl)phenyl] methanone	a-(cyclopropylcarbonyl)- 2-(methylsulfonyl)- b-oxo-4-(trifluoromethyl) benzenepropanenitrile
Molecular Weight (g/mol)	359	359
Water Solubility (mg/l)	6.2	326
Octanol-Water Partition Coefficient (log <i>P</i>)	2.32	-0.37
Vapor Pressure (mmHg)	1.0×10^{-6} at 25°C	1.0×10^{-6} at 25°C
Soil K_{oc} (cm ³ /g)		
Range	102-227	62-204
Mean \pm 90% Confidence Interval	155 \pm 35	139 \pm 23
Laboratory Aerobic Soil Half-Life (days)		
Range	0.3-4.3	10-39
Mean \pm 90% Confidence Interval	1.7 \pm 0.9	27.0 \pm 7.0
Field Dissipation Half-Life (days)		
Range	0.5-3.7	7.0-79.0
Mean \pm 90% Confidence Interval	2.0 \pm 0.4	18.0 \pm 7.0
Hydrolysis Half-Life at pH = 7 (days)	0.84	Stable
Dissipation Half-Life from Water Phase in Sediment/Water System (days)	0.5-0.6	66-89
Aquatic Photolysis Half-Life (Natural Sunlight) at pH = 7 (days)	6.7	Stable

is a pigment inhibitor. The biochemical target of isoxaflutole is the inhibition of 4-hydroxyphenylpyruvate dioxygenase (HPPD). HPPD bleaches young leaf tissue in susceptible weeds (Pallett *et al.*, 1998; USEPA, 1998). Isoxaflutole rapidly degrades (i.e., half-life, $t_{1/2}$, ~two days) into the actual inhibitor of HPPD: RPA 202248. This daughter product is a more persistent with a $t_{1/2}$ >25 days (Table 1). In general, the mobility of isoxaflutole is restricted in silty clay and loam soils in that it is generally retained at the soil surface where it can be taken up by surface-germinating weed seeds. RPA 202248, due to its greater solubility, is potentially mobile (USEPA, 1998).

The first experimental site was a 30.4 ha isolated field in Allen County, Indiana, with Hoytville silty clay and slopes <2%. Fox *et al.* (2004) used data from this field site in proposing their EF modification. The second experimental site was a 10.9-ha field in Owen County, Indiana, with Philo silt loam soils and slopes <1%. Both fields contained pattern subsurface drain lines (polyurethane pipes) with 10 m spacing with a depth of 0.9-1.2 m and running east-west that connected to a drain system emptying at the northeast and southeast corners of the fields. A sampler was located at both the northeast and southeast corners of the fields. Subsurface drainage from the sites flowed into ditches that then discharged into the Maumee River for the Allen County site and the west fork of the White River for the Owen County site.

No till agricultural management practices were used at both sites in an annual corn (1998 and 2000) and soybean (1999) rotation. Both fields were planted to corn on May 25, 2000. Weather stations recorded hourly temperature, relative humidity, solar radiation, wind speed and direction, and rainfall during the 2000-growing season. Soil samples collected at both sites were analyzed for particle size distribution, organic matter content, and bulk density. Soil samples were collected every 15 cm from the soil surface to ~1.5 m below the soil surface (Table 2).

A potassium bromide tracer was dissolved in water and surface applied at the rate of 39.2 kg/ha on April 29, 2000 (day 120) for the Allen County site and at the rate of 37.7 kg/ha on May 15, 2000 (day 135), for the Owen County site. Isoxaflutole was surface applied pre-emergent to bare soil in solid form at the rate of 0.13 kg/ha five days after bromide application in the Allen County field and one day after bromide application in the Owen County field. Concentrations in soil and subsurface drain flow were monitored for the remainder of the growing season.

Soil samples were collected periodically during six months following application to quantify the distribution of bromide (Br) and isoxaflutole within the soil profiles. Core samples were obtained to a depth of 1.8 m. The fields were divided into four quadrants and sampling locations were selected using a random number generator. Four cores were collected using the bucket-auger technique. Cores from only the top 15 cm were collected for the first five days after the tracer application. On subsequent samplings, the entire soil profile was sampled and cores within a quadrant were composited.

Flow from the drain outlets was measured for the duration of the sampling period. Tile drain flow was measured using Isco Model 730 Bubble Flow Meters (Isco, Inc., Lincoln, Nebraska). Flows were recorded every 30 minutes. For the Allen County site, data for late-season high flow events were missing due to flooding of the sampling site. Therefore, only flow on the recession limbs (i.e., following a high subsurface flow event) was available for the Allen County site during the last half of the growing season. For the Owen County site, instrument malfunction prevented collection of flow data. As Br is a conservative tracer, Br concentration data indicated flow conditions at the Owen County site.

Multiple water samples from edge of the fields' subsurface drain flow were collected daily for the remainder of the year. The water samples were

TABLE 2. Soil Texture, Organic Matter, and Bulk Density as Measured From Soil Samples for the Allen County, Indiana, and Owen County, Indiana, Sites.

Layer	Depth (cm)	Soil Type	% Clay	% Sand	Organic Matter (%)	Bulk Density (g/cm ³)
Allen County, IN						
1	15	Clay	43	25	3.02	1.17
2	30	Clay	43	25	2.73	1.18
3	107	Clay	47	25	1.10	1.18
4	152	Clay	45	26	0.83	1.17
Owen County, IN						
1	15	Loam	14	30	1.63	1.13
2	30	Loam	14	30	1.08	1.13
3	90	Loam	12	32	0.62	1.17
4	107	Loam	12	32	0.30	1.21
5	152	Loam	12	32	0.23	1.14

analyzed to determine the extent of leaching to the drainage system. The drain sampling points were selected where the subsurface drain systems empty into the collector ditches. The drain outlets were modified to allow use of an automated sampling device. A sample pickup was placed where the drains were first exposed at the ditch bank. An Isco model 6700 sampler (Isco, Inc.) was installed at each drain and programmed to collect a water sample every 80 minutes (18 samples every 24-hours period). Each day the filled sample bottles were collected and new empty bottles placed in the automated sampler. The freshly collected samples were labeled, dated, and placed in frozen storage.

Bromide tracer samples were analyzed using "Method of Analysis Number 21, Determination of Potassium Bromide Residues in Ground Water, Revision 1.0, March 31, 1999" (a modification of EPA Method 300.0, Determination of Inorganic Anions by Ion Chromatography, Revision 2.1 dated August 1993). Soil samples were extracted with 100 ml of high-performance liquid chromatography (HPLC) grade water after thawing and then centrifuged. An aliquot of the extract was then diluted with HPLC grade water prior to analysis by ion chromatography. The limit of detection of the method is 0.1 mg/l. Water samples were analyzed for isoxaflutole and RPA 202248 using "Method of Analysis for the Quantification of Isoxaflutole and Its Metabolites in Water Using Isotopically Labeled Internal Standards-Revision 99.3" (April 18, 2000; File Number 46037). The limit of quantification is 0.010 µg/l. The limit of detection is 0.003 µg/l. Samples were fortified with ¹³C labeled standards. Isoxaflutole and RPA 202248 were extracted from water using a RP-102 resin cartridge (Applied Separations, Allentown, Pennsylvania) and then removed with acetonitrile:methanol. All residue analysis was accomplished by LC-MS-MS (Applied Separations) using a C-18 column. The typical analytical set included 4-20 field samples, at least one untreated control sample, and at least one fortified procedural recovery sample. Each set of sample injections was bracketed by calibration standard injections of appropriate analyte concentrations.

Root Zone Water Quality Model (RZWQM)

RZWQM can simultaneously simulate pesticide and metabolite fate and transport, preferential flow, and artificial subsurface drainage (Ahuja *et al.*, 2000a). The model divides water flow processes into two phases: (1) infiltration into the soil matrix and macropores with macropore-matrix interaction and (2) redistribution of moisture in the soil matrix (Ahuja *et al.*, 2000b). The infiltration of water through

a layered soil profile is modeled using a modified Green-Ampt approach. The model routes precipitation that exceeds the infiltration rate into macropores based on a flow capacity limit determined by Poiseuille's law (Malone *et al.*, 2003). The model then evenly distributes water entering into macropores among the number of effective macropores per unit area. RZWQM models potential evaporation and transpiration using a modified form of the Shuttleworth and Wallace (1985) double layer model. The fundamental improvement provided by RZWQM as opposed to other pesticide transport models (i.e., GLEAMS and PRZM) is the ability to simulate individual precipitation events and processes during events on a subdaily time scale (Wauchope *et al.*, 2000).

Wauchope *et al.* (2004) reviewed the pesticide processes module of RZWQM. The model uses a nonuniform mixing approach to model chemical transfer to overland flow (Ahuja *et al.*, 2000b). Chemical transport in the matrix is modeled using a partial piston displacement, partial mixing approach. Redistribution of soil water is modeled using a mass conservative numerical solution of Richard's equation, which includes plant uptake, surface evaporation, fluctuating water table, and tile flow (Johnsen *et al.*, 1995). The pesticide submodel within RZWQM assumes dissipation processes in crop foliage, crop residues, soil surface, and soil subsurface (Ahuja *et al.*, 2000b). RZWQM adjusts the rate constants for surface and subsurface dissipation of pesticides for temperature (T) and soil water content (θ) according to the following equation (Ma *et al.*, 2004):

$$k(T, \theta) = k(T_r, \theta_r) \exp \left[\frac{E_a}{R} \left(\frac{1}{T_r} - \frac{1}{T} \right) \right] \left(\frac{\theta}{\theta_r} \right)^\beta, \quad (1)$$

where $k(T, \theta)$ is the rate constant at the specified T and θ , $k(T_r, \theta_r)$ is the rate constant at the reference T and θ , E_a is the activation energy, and R is the universal gas constant and β is a constant. RZWQM only simulates transformation in one compartment (foliage, residue, soil surface, or subsurface). A transformation process was specified (e.g., assumed to be aerobic biodegradation in soil), which generated the daughter product based on the specified reaction rate constant and based on a specified transformation fraction or the fraction of parent degradate that forms daughter product, assumed to be 100% in this research (Table 1). On a daily time step, the RZWQM adds the daughter product to the existing amounts in each soil layer by calculating their production by this specified transformation process.

Allen County Site

Fox *et al.* (2004) calibrated a RZWQM model based on observed drain flow for the Allen County site and a one-year (January 1, 2000, through December 31, 2000) simulation period (Table 3). We followed the same approach in this research with a simulation period of the entire 2000-growing season. The soil profile was divided into five layers for input into RZWQM: 0-15, 15-30, 30-107, 107-152, and 152-296 cm. Management practices for the field were entered into the model including the applications of KBr and ISO. Weather data for the entire 2000-growing season were input based on measured hourly data from the weather station.

The model was calibrated by adjusting the modified Brooks and Corey (1964) parameters, vertical saturated conductivity, and lateral saturated conductivity until model predictions matched observed subsurface drainage collected during the experiments from Day 120 to 190 of the 2000-growing season. Several peaks in the subsurface drain flow were not available due to instrument error. However, many of the early peaks were available and the ability of the model to predict remaining peaks could be accessed qualitatively based on precipitation hyetographs. Soil parameter values were constrained to be within limits reported by the Map Unit Use File (MUUF) soils database. Calibration continued by trial-and-error until the sum of squared errors between observed and measured subsurface drain flow were minimized.

After the calibration on hydrology, Fox *et al.* (2004) evaluated the model based on predicted bromide and isoxaflutole in subsurface drain flow using the mean

pesticide parameters (Table 1). In this research, parent and metabolite fate and transport were evaluated by comparing observed concentrations of isoxaflutole and RPA 202248 in edge of field subsurface drain flow to predicted concentrations based on linear regression with and without the EF modification. Model evaluation was also based on an acceptance criterion as quantified by a normalized objective function (NOF) (Kornecki *et al.*, 1999). This function is the ratio of the standard deviation of differences to the overall mean (X_a) of the observed parameter

$$\text{NOF} = \frac{\text{STDD}}{X_a} = \frac{\sqrt{\frac{\sum_{i=1}^n (x_i - y_i)^2}{n}}}{X_a}, \quad (2)$$

where x_i and y_i are the i th observed and predicted values, respectively. For screening applications, where parameters are not calibrated for the site, model results should be within an order of magnitude of the observed values, which corresponds to an NOF value of 9.0; for a site-specific application where data are measured on-site, the model should match observations within a factor of 2.0, which corresponds to an NOF value of 1.0 (Pennell *et al.*, 1990; Loague and Green, 1991; Hession *et al.*, 1994). The NOF has been used in past literature for similar model evaluations and comparisons (Pennell *et al.*, 1990).

Owen County Site

This research also applied RZWQM to the Owen County field site with a one-year (January 1, 2000,

TABLE 3. Default and Calibrated RZWQM Soil Hydraulic Parameters Derived From Input Soil Texture and Bulk Density for the Allen County, Indiana, Site.

Layer	Depth (cm)	Moisture Contents [†] (cm ³ /cm ³)				$K_{\text{sat}}^{\ddagger}$ (cm/h)	Brooks-Corey Parameters [§]		
		θ_r	θ_s	θ_{33}	θ_{15}		S_2 (cm)	A_2	N_2
Default Parameters									
1	15	0.09	0.48	0.38	0.27	0.06	37	0.13	2.15
2	30	0.09	0.48	0.38	0.27	0.06	37	0.13	2.15
4	107	0.09	0.48	0.38	0.27	0.06	37	0.13	2.15
5	152	0.09	0.48	0.38	0.27	0.06	37	0.13	2.15
6	296	0.09	0.48	0.38	0.27	0.06	37	0.13	2.15
Calibrated Parameters									
1	15	0.09	0.48	0.38	0.27	1.0	5	0.05	2.15
2	30	0.09	0.48	0.38	0.27	0.5	5	0.05	2.15
4	107	0.09	0.48	0.38	0.27	0.3	5	0.05	2.15
5	152	0.09	0.48	0.38	0.27	0.1	5	0.05	2.15
6	296	0.09	0.48	0.38	0.27	0.1	5	0.05	2.15

Notes: Values reported in Fox *et al.* (2004); RZWQM, Root Zone Water Quality Model.

† θ_r and θ_s are the residual and saturated moisture contents; and θ_{15} and θ_{33} are the moisture contents at 1,500 and 333 kPa tension.

‡ K_{sat} is the vertical saturated conductivity; K_{lat} , the lateral saturated hydraulic conductivity was assumed three times K_{sat} .

§ S_2 is the bubbling pressure head on the moisture distribution curve; A_2 is the pore size distribution index; and N_2 is the exponent for the unsaturated conductivity curve.

through December 31, 2000) simulation period. Based on soil samples, the soil profile was divided into five layers: 0-15, 15-30, 30-90, 90-107, and 107-152 cm. A sixth layer was added to simulate a confining layer below 152 cm. Based on input soil texture and bulk density, RZWQM derived default hydraulic parameters such as vertical and lateral saturated hydraulic conductivity, field capacity, and water retention parameters (Table 4). These default parameters were used initially to determine the capability of the model to predict flow and transport without site-specific data.

Additional soil parameters were available from the MUUF soil database (Baumer *et al.*, 1987; Rawls *et al.*, 2001) for Philo silt loam. Data from the soil database matched laboratory measurements of soil texture, organic matter, and bulk density from the field samples. Default surface crust conductivity and soil macroporosity parameters, including the macropore radius, effective macroporosity, and lateral sorptivity reduction factor, were obtained from selected literature (Ahuja *et al.*, 1995; Malone *et al.*, 2003). The same macropore parameters were input for all depths. Management practices for the field were entered into the model including the applications of potassium bromide and isoxaflutole. Weather data were input based on measured hourly data from the weather station. Initially, no direct connection was assumed between macropores and subsurface drainage (i.e., EF = 0%).

The model was calibrated by adjusting the soil hydraulic parameters within limits established by the MUUF soil database and soil samples until model

predictions matched observed bromide (Br) concentrations. As Br is a conservative tracer, calibrating the model to observed Br in subsurface drain flow is equivalent to calibration to flow data. The primary variables adjusted during calibration were the Brooks and Corey (1964) parameters, vertical saturated conductivity, lateral saturated conductivity, and soil-water retention parameters [the residual (θ_r) and saturated (θ_s) moisture contents and the moisture contents at 1,500 and 333 kPa tension]. After calibration on Br, isoxaflutole, and RPA 202248 transport through the soil matrix and macropores was simulated using the calibrated model and the mean pesticide parameters (Table 1). Observed concentrations of isoxaflutole and RPA 202248 in edge of field subsurface drain flow were compared with predicted concentrations based on linear regression and NOF with and without the EF modification. An EF of 2% was assumed to evaluate the transferability of this parameter at this additional field site.

Long-Term Annual Loss Simulations

The calibrated RZWQM models for Allen County and Owen County were used to conduct long-term simulations with 30 years of weather data. Simulation runs were based on the SAMPSON weather data for the stations closest to the sites (USEPA, 2003). Model simulations predicted 30-year distributions of percent annual mass loss of isoxaflutole and RPA 202248 in terms of mass of isoxaflutole applied. Average predicted percent loss over the 30-year period

TABLE 4. Default and Calibrated RZWQM Soil Hydraulic Parameters Derived From Input Soil Texture and Bulk Density for the Owen County, Indiana, Site.

Layer	Depth (cm)	Moisture Contents [†] (cm ³ /cm ³)				$K_{\text{sat}}^{\ddagger}$ (cm/h)	Brooks-Corey Parameters [§]		
		θ_r	θ_s	θ_{33}	θ_{15}		S_2 (cm)	A_2	N_2
Default Parameters									
1	15	0.027	0.574	0.234	0.116	1.32	3.98	0.22	2.66
2	30	0.027	0.574	0.234	0.116	1.32	3.98	0.22	2.66
3	90	0.027	0.558	0.234	0.116	1.32	4.55	0.22	2.66
4	107	0.027	0.543	0.234	0.116	1.32	5.18	0.25	2.66
5	152	0.027	0.570	0.234	0.116	1.32	4.11	0.22	2.66
6	296	0.075	0.464	0.312	0.136	0.23	25.80	0.19	2.58
Calibrated Parameters									
1	15	0.015	0.574	0.286	0.136	0.68	5.00	0.21	2.63
2	30	0.015	0.574	0.286	0.136	0.68	5.00	0.21	2.63
3	90	0.015	0.558	0.286	0.136	0.68	5.00	0.21	2.63
4	107	0.015	0.543	0.286	0.136	0.68	5.00	0.21	2.63
5	152	0.015	0.570	0.286	0.136	0.68	5.00	0.21	2.63
6	296	0.075	0.464	0.312	0.136	0.23	25.80	0.19	2.58

Notes: RZWQM, Root Zone Water Quality Model.

[†] θ_r and θ_s are the residual and saturated moisture contents; and θ_{15} and θ_{33} are the moisture contents at 1,500 and 333 kPa tension.

[‡] K_{sat} is the vertical saturated conductivity; K_{lat} , the lateral saturated hydraulic conductivity was assumed three times K_{sat} .

[§] S_2 is the bubbling pressure head on the moisture distribution curve; A_2 is the pore size distribution index; and N_2 is the exponent for the unsaturated conductivity curve.

was compared with isoxaflutole and RPA 202248 percent loss from sites without subsurface drainage as reported by Rector *et al.* (2003).

RESULTS AND DISCUSSION

Allen County Site

Results for hydrology and bromide have been discussed previously by Fox *et al.* (2004). The calibrated model (Table 3) captured the dynamics of the leaching when simulating concentrations of isoxaflutole (Figure 1) and RPA 202248 (Figure 2), but the amplitude of the peaks was less well reproduced in edge of field subsurface drain flow at the Allen County site. Rainfall controlled the occurrence of parent and metabolite in subsurface drain flow, especially for early peaks in drain flow concentration due to macropore flow. Without an EF, the model significantly underpredicted the initial peaks in isoxaflutole and RPA 202248 concentrations with an NOF of 1.2 for both and R^2 of approximately 0.10 and 0.15, respectively. When assuming an EF of 2%, the model was able to capture these concentrations (Figures 1 and 2). A linear regression between predicted and observed isoxaflutole and RPA 202248 resulted in slopes of 0.81 and 0.30, intercepts of 0.01 and 0.70, and R^2 of 0.60 and 0.34, respectively. NOF for isoxaflutole and RPA 202248 were 0.9 and 1.0, respectively. For the maximum RPA 202248 concentration peak on day 131, the RZWQM underpredicted the average measured concentration by 92.5% without an

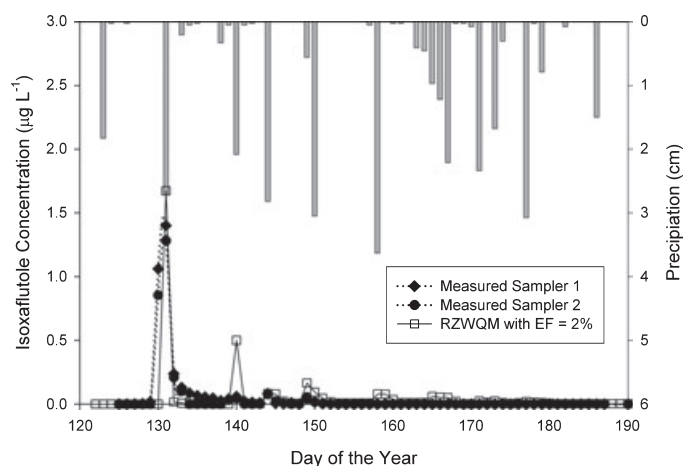


FIGURE 1. Comparison of Measured and Root Zone Water Quality Model (RZWQM) Simulated Isoxaflutole Concentrations in Edge of Field Subsurface Drain Flow With an Express Fraction of 2% for the Allen County, Indiana, Site.

EF and by only 43.0% with an EF of 2%. The peak isoxaflutole also occurred on day 131 and was underpredicted by RZWQM by 93.0% without an EF and overpredicted by 24.6% with an EF of 2%.

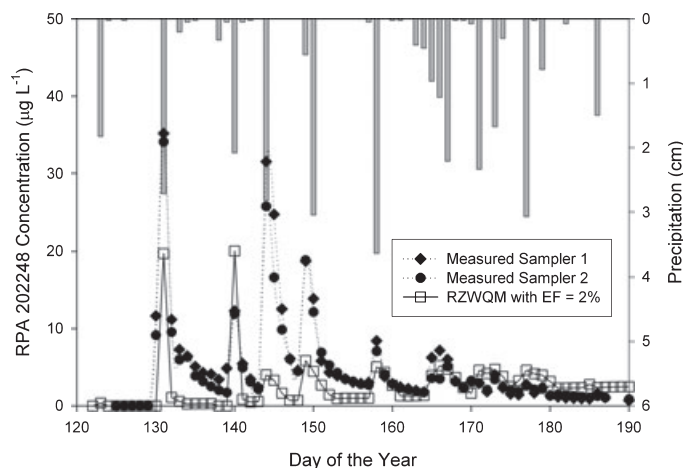


FIGURE 2. Comparison of Measured and Root Zone Water Quality Model (RZWQM) Simulated Isoxaflutole Metabolite (RPA 202248) Concentrations in Edge of Field Subsurface Drain Flow With an Express Fraction of 2% for the Allen County, Indiana, Site.

As verified in the field by Shipitalo and Gibbs (2000) and laboratory by Akay and Fox (2006), macropores located within 20-50 cm of the drain tiles will transmit flow and pesticide directly into the drain line. This is currently being accounted for in the EF modification in that an EF of the water/pesticide reaching the water table is diverted directly into the tile line.

Discrepancies between observed and model predicted RPA 202248 were primarily due to the inability of the model to capture the third (day 144) and fourth (day 149) peaks in RPA 202248 concentration. The model also had difficulty in predicting concentrations on the recession limbs of drainage hydrographs (Figures 1 and 2). Fox *et al.* (2004) report similar observations for bromide predictions. Failure of the model to capture the peak RPA 202248 concentrations on days 144 and 149 was not a product of direct macropore connection with subsurface drainage. Fast breakthrough by drain-connected macropores only influences breakthrough when concentration differences between the macropore and matrix flow domains were large (Fox *et al.*, 2004). In this case, there was little difference between macropore and matrix concentrations.

Predicted percent mass loss of isoxaflutole in edge of field subsurface drain flow in terms of mass applied was <1.0% for isoxaflutole and approximately 5.3% for RPA 202248, resulting in a cumulative simulated percent mass loss of approximately 5.4%. Total observed mass loss in drainage was not available due

to flow data missing for high flow events. However, as the model simulations matched observed flow data and pesticide concentrations, especially the peaks, simulated annual loss should theoretically match observed percent loss. In fact, a distinct advantage of calibrated models is being able to estimate missing observations for completing a chemical mass balance. Simulated cumulative drainage losses were comparable with isoxaflutole/RPA 202248 losses in runoff on nondrained plots (4.4–8.5%) as observed by Rector *et al.* (2003). Predicted mass loss through runoff was insignificant (i.e., <0.5% for isoxaflutole and <1.0% for RPA 202248) compared with mass loss through subsurface drainage. In terms of mass of isoxaflutole applied, the largest simulated loss based on a chemical mass balance occurred through chemical degradation, which accounted for over 98% of the total loss. RPA 202248, formed from this chemical degradation, primarily degraded within the soil profile, with chemical degradation accounting for approximately 90% of the total mass of RPA 202248 formed from isoxaflutole. Storage of isoxaflutole and RPA 202248 within the soil profile was insignificant at the end of the year.

Owen County Site

For the Owen County site, RZWQM predicted the pattern of bromide concentrations in edge of field subsurface drain flow using RZWQM default hydraulic parameters and EF = 0%, but failed to capture the two primary peaks in observed Br concentration shortly after application (Figure 3). Minimal calibration of

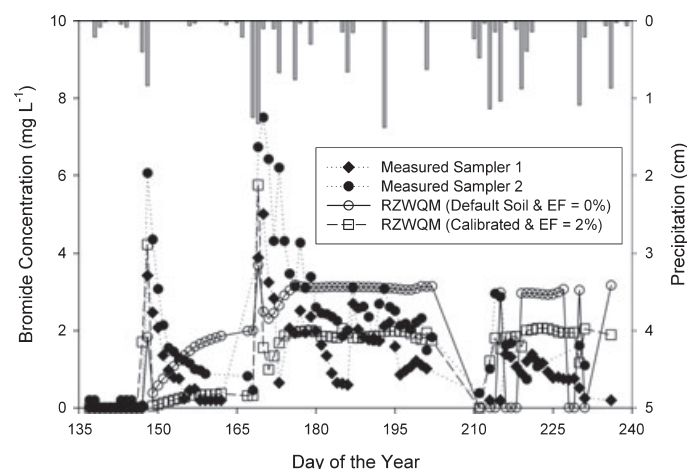


FIGURE 3. Comparison of Measured and Root Zone Water Quality Model (RZWQM) Simulated Bromide Concentrations in Edge of Field Subsurface Drain Flow With Default RZWQM-Derived Soil Hydraulic Parameters and an Express Fraction, EF = 0% and Calibrated Soil Hydraulic Parameters and EF = 2% for the Owen County, Indiana, Site.

hydraulic parameters improved the predicted temporal distribution of bromide in edge of field subsurface drain flow (Table 4). Vertical, saturated conductivities were reasonable compared with the MUUF soil database that suggested hydraulic conductivities between 0.5 and 5.0 cm/h. Lateral, saturated conductivities were three times greater than the vertical conductivity, similar to the default RZWQM parameters.

The model was capable of simulating these early peaks when using EF of 2%, similar to the value used at Allen County (Figure 3). The 2% EF is justified based on the field and laboratory observations that macropores located within 20–50 cm of drain lines are “hydrologically” directly connected (Shipitalo and Gibbs, 2000; Akay and Fox, 2006). This 20–50 cm area represents approximately 2–5% of the field. With an EF = 2%, linear regression predicted an R^2 of 0.31 and the NOF was 0.8 suggesting that the model met the site-specific criterion for bromide and therefore was appropriately calibrated based on hydrologic response.

The calibrated model was able to capture the timing of one peak in isoxaflutole (Figure 4) and two peaks in RPA 202248 (Figure 5) when including an EF of 2%. Simulated isoxaflutole and RPA 202248 concentrations were consistently less than observed concentrations at these peaks. Not including an EF once again consistently underpredicted peak concentrations shortly after application with an R^2 of <0.1 for isoxaflutole and metabolite. NOF values were 3.5 for isoxaflutole and 2.7 for metabolite (Figures 4 and 5). Linear regression resulted in an R^2 of 0.44 and 0.10 for isoxaflutole and RPA 202248, with NOF values of 1.5 and 1.7, respectively, when including an

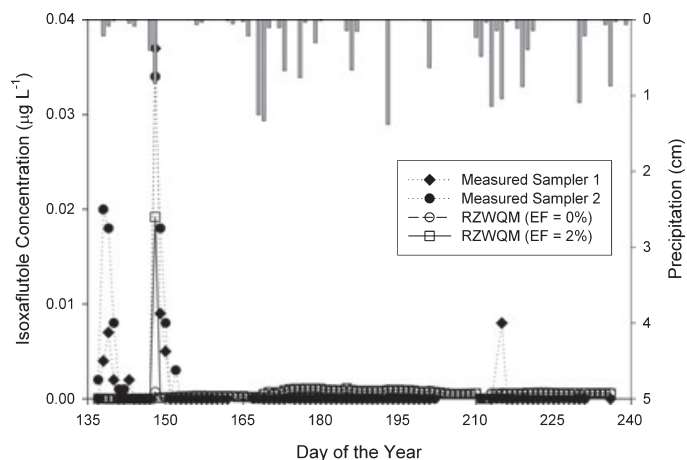


FIGURE 4. Comparison of Measured and Root Zone Water Quality Model (RZWQM) Simulated Isoxaflutole Concentrations in Edge of Field Subsurface Drain Flow With Express Fractions, EF = 0 and 2% for the Owen County, Indiana, Site.

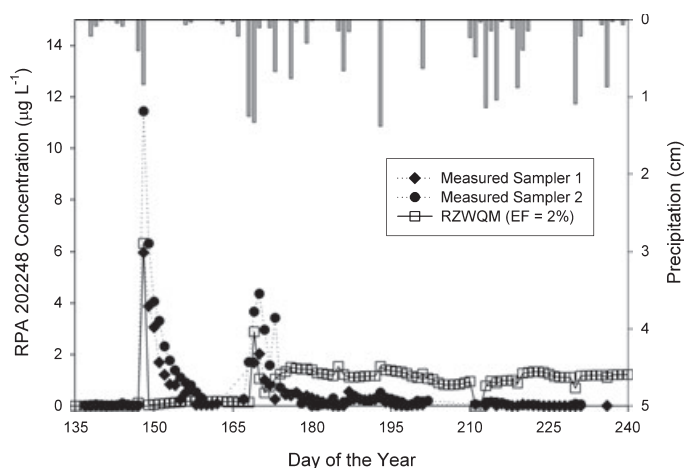


FIGURE 5. Comparison of Measured and Root Zone Water Quality Model (RZWQM) Simulated Isoxaflutole Metabolite (RPA 202248) Concentrations in Edge of Field Subsurface Drain Line With an Express Fraction of 2% for the Owen County, Indiana, Site.

EF of 2%. As pesticide fate and transport properties were not calibrated, these NOF values were deemed acceptable. The maximum concentration peak for both parent and metabolite occurred on day 148. The RZWQM underpredicted the peak parent concentration by 97.5% with an EF of 0% but by only 30.9% with an EF of 2%. For metabolite, the RZWQM underpredicted the peak concentration by 94.4% without an EF and slightly (i.e., 28%) underpredicted the peak concentration with an EF of 2%.

The magnitudes of the peaks could be simulated by increasing the EF. Therefore, the underprediction of these peaks with a 2% EF suggests that calibration may be necessary for different field sites, but generally should fall within the field reported range of 2–5% (Shipitalo and Gibbs, 2000). Calibration suggested an EF of 4%. With an EF of 4%, the RZWQM predicted the first concentration peak (8.8 µg/l) on day 148 in between the measured concentrations (6.0–11.4 µg/l) and was approximately equal to the maximum observed concentration on day 170 (i.e., predicted of 4.6 µg/l compared with observed of 4.4 µg/l). For an EF of 5%, the RZWQM predicted concentrations of 10.5 and 5.5 µg/l on days 148 and 170, respectively.

Confirming the results from Allen County, the model continued to fail to match the temporal distribution of several individual subsurface drainage events, especially on the recession limbs of drainage hydrographs (Figures 4 and 5), with percent differences approximately 70–90% between simulated and measured concentrations after the first concentration peak. The model captured one of the two significant peaks in observed isoxaflutole concentration (Figure 4) but failed to predict an observed isoxaflutole concen-

tration peak one day after application (day 138). This peak occurred during a 0.5-cm rainfall event. Concentrations in edge of field subsurface drain flow one day after application were most likely due to preferential transport through macropores. However, the model failed to simulate macropore flow for this rainfall event. For this storm event, predicted antecedent moisture at the soil surface allowed soil matrix infiltration instead of macropore flow. As the difficulty in simulating this immediate peak concentration was due to the model simulating precipitation infiltration and not macropore flow, increasing EF had no impact on predicted bromide or isoxaflutole concentrations on day 138. The RZWQM simulations also predicted a leveling of parent and metabolite concentrations in subsurface drain flow that were not apparent in observed concentrations. It is hypothesized that predicted concentrations after day 180 were the result of the model underpredicting the two concentration peaks soon after application. It should be noted, however, that the predicted isoxaflutole concentrations are <0.005 µg/l and the predicted RPA 202248 concentrations are approximately 1.0 µg/l.

Predicted percent mass loss of isoxaflutole in edge of field subsurface drain flow in terms of mass applied was <0.1% for isoxaflutole and approximately 4.3% for RPA 202248, resulting in a simulated cumulative percent mass loss of approximately 4.3%. Predicted mass loss of isoxaflutole or RPA 202248 through runoff was insignificant (i.e., <0.1%). As expected, the primary loss of isoxaflutole occurred through chemical degradation (>99% of the total mass applied at the end of the year). Chemical degradation also accounted for the mass loss of RPA 202248 (i.e., >93% of the total mass of RPA 202248 formed from isoxaflutole). Storage of isoxaflutole and RPA 202248 within the soil profile was insignificant at the end of the year. The cumulative percent drainage loss in subsurface drained fields was comparable with percent loss in runoff for nondrained fields as reported by Rector *et al.* (2003). For the nondrained field site studied by Rector *et al.* (2003) and the Owen County site, soil texture and slope were similar.

Long-Term Annual Loss Simulations

Thirty-year distributions of annual loss of isoxaflutole and RPA 202248 in edge of field subsurface drain flow suggest that losses are no greater than losses by runoff. Annual minimum, maximum, and average cumulative loss as percent of isoxaflutole applied for the 1961–1990 30-year simulations were 1.19, 5.66, and 3.04%, respectively, for the Allen County site and 0.28, 4.67, and 1.31%, respectively, for the Owen County site. Cumulative mass losses during the 2000

field studies (5.41% for Allen County and 4.26% for Owen County) were in the upper range of these distributions. These percentages correspond to isoxaflutole/RPA 202248 losses as percent of isoxaflutole applied reported by Rector *et al.* (2003) in nondrained fields (i.e., runoff studies) on fields with similar slopes. The Rector *et al.* (2003) study also possessed similar soils (i.e., both silt loam) to the Owen County site.

DISCUSSION

The underprediction of the peak and recession limb concentrations for both parent and metabolite suggests that calibration on pesticide properties and direct connectivity parameters (i.e., EF) may be required and more sophisticated techniques for accounting for macropore/subsurface drain interconnectivity are required in terms of chemical routing. The failure to match pesticide concentrations on the recession limbs of drainage hydrographs is most likely due to the placement of remaining water and chemical (after routing the EF directly into drain lines) on the top of the water table in the one-dimensional RZWQM. For example, for macropores between 50 and 100 cm from the subsurface drain, pesticide should be diverted into the soil profile to lower depths depending on the height of the water table above the drain line at that location, such as what is predicted by the Hooghoudt equation. Therefore, a macropore at 75 cm from the drain line transmits pesticide to the soil layer at the water table depth at 75 cm from the drain line. A macropore at 100 cm away from the drain line diverts pesticide to a water table depth that is closer to the ground surface than the water table depth for the macropore that is 75 cm from the drain line. An improved procedure is needed to distribute the pesticide across the soil profile in a quasi-two-dimensional fashion as opposed to the one-dimensional approach of the current EF modification.

An alternative to simulating metabolite formation from parent compound degradation is simulating the metabolite as the sole pesticide with an application rate equal to the application rate of the parent compound (i.e., assuming complete transformation). For both the 2000-field tests at Allen County and Owen County, model simulations with only the daughter product predicted slightly higher concentrations (generally $<2 \mu\text{g/l}$) of RPA 202248 in subsurface flow compared with modeling approaches based on simultaneously predicting parent and metabolite fate and transport. The slightly higher concentrations were due to the model not accounting for possible parent

compound loss through macropore transport to the drains. The parent compound did reach subsurface flow in one large peak concentration shortly after application and therefore affected the relative concentration of RPA 202248 formed at the soil surface and therefore in the soil profile. For parent compounds with half-lives smaller than that of isoxaflutole, assuming complete transformation into metabolite would be reasonable. However, simultaneously predicting parent and metabolite fate, transport, and dissipation would be necessary for parent compounds with longer half-lives.

The RZWQM limits transformation to only one compartment (i.e., residue, soil surface, or soil profile). This limitation results in slight errors for daughter product concentrations. For this scenario, the errors are more than likely insignificant due to the rapid breakdown of isoxaflutole in the soil. However, these errors will amplify with parent compounds that potentially degrade in multiple compartments. Pesticides with longer half-lives can be transported into subsurface zones through macropore flow and then degrade in the subsurface leading to combined daughter product formation in both the surface and subsurface compartments. Users of such pesticide transport models need to be aware of such limitations.

SUMMARY AND CONCLUSIONS

The significance of pesticide metabolites in the environment has become increasingly emphasized among regulators and interest groups. However, few, if any, studies in the literature report evaluations of pesticide transport models for both parent compounds and metabolites in artificially drained, subsurface systems. The objective of this research was to perform such an evaluation using RZWQM. This research evaluated the model for pesticide fate and transport studies at two artificially subsurface drained field sites in Allen County and Owen County. The parent compound was isoxaflutole, the active ingredient in BALANCE[®] herbicide, which degraded rapidly (i.e., a half-life of less than two days) into a metabolite, RPA 202248.

The RZWQM simulated both parent and metabolite transport within artificially, drained soils with minimal calibration and assuming transformation in only one compartment. The model was able to capture the simultaneous transport and transformation of the parent compound into its metabolite and then the resulting transport and degradation of the metabolite. The model consistently underpredicted parent

and metabolite concentrations when not accounting for direct connection between macropores and subsurface drains. Including a direct connection improved model results for the peak concentrations in parent and metabolite compounds soon after application of the parent pesticide. The idea that macropores located within 50 cm of the drain tiles will transmit flow and pesticide directly into the drain line is currently being accounted for in the EF modification. By including the Owen County field site and comparing results from the Allen County site, this research evaluated the transferability of the EF parameter. An EF of 2% improves the model predictions for both field sites but users may need to calibrate this parameter for field-specific conditions to improve the prediction of concentration peaks.

The RZWQM was capable of predicting trends in parent and metabolite concentrations in edge of field subsurface drains. However, the model did not consistently predict concentrations that matched observations on the recession limbs of individual subsurface flow drainage events (with percent differences approximately 70-90% between simulated and measured concentrations after the first concentration peak). The inability to capture recession limb concentrations consistently at the two field sites suggests that the EF modification only partially accounts for the direct connectivity phenomenon and additional modifications are necessary to capture the physical processes involved during preferential flow.

Simulated cumulative percent mass loss of isoxaflutole and RPA 202248 in terms of mass of isoxaflutole applied was approximately 5.4 and 4.3% for the Allen County and Owen County sites, respectively, for the 2000 study period. Thirty-year simulations using the calibrated models for both sites predicted percent mass loss of isoxaflutole/RPA 202248 that matched reported isoxaflutole/RPA 202248 losses in surface runoff on nondrained sites of similar slope and soil type.

Assuming complete transformation of parent to metabolite failed to account for loss of the parent compound in rainfall events shortly after application. This can be significant even in a case where the parent compound has a half-life of approximately two days. The interaction of parent and daughter compounds is important, especially when considering the possible presence of multiple degradation products from a number of agrochemicals in intensive agricultural areas. Therefore, quantifying the combined environmental exposure of parent pesticides and their metabolites requires models capable of simultaneously simulating multiple species transport through numerous hydrologic pathways, transformation, and degradation.

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